

An example of an iron (III) porphyrin with spin mixed ground state

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Abstract. The paper reports synthesis and physical characterisation of a new iron(III) porphyrin which shows unusual features of quantum mechanically mixed ground state in its magnetic properties. Magnetic susceptibility (300–3·6 K) and Mössbauer spectroscopy (300–77 K) studies of the compound are described and discussed with reference to some bacterial ferricytochrome C' exhibiting similar spin-mixed ground state.

Keywords. Iron(III); porphyrin; magnetic susceptibility; Mössbauer spectroscopy; spin mixed ground state.

1. Introduction

A ferric ion (d^5 electron configuration) can exist in three discrete spin states, $S = 5/2$, $1/2$ and $3/2$. For iron(III) heme systems the $S = 3/2$ spin state is rather uncommon, the $S = 5/2$ and $S = 1/2$ being the usual ones. There is also a possibility of thermal spin equilibrium between these spin states (George *et al* 1964; Martin and White 1968) and/or quantum mechanical mixing of spin states (Harris 1966, 1968a, 1968b; Maltempo 1974). The quantum mechanical mixing of spin states in ferric porphyrins (and heme systems) refers to a situation in which the wave function of the electronic ground state of the ferric ion contains a substantial contribution from two or more different iron spin states. In contrast to the thermal spin equilibrium in which the ferric porphyrin molecule can be monitored in two magnetically distinguishable pure spin states, a molecule having quantum mechanically mixed spin states would correspond to a single magnetic species with magnetic properties different from those corresponding to either of the pure spin states. In ferric heme systems the most important mechanism for mixing

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of the spin states is spin-orbit coupling governed by the selection rule : $\Delta S = 0, \pm 1$ and $\Delta S_z = 0, \pm 1$ (Griffith 1961). Thus, while $S = 3/2$ can be mixed to first order with either $S = 5/2$ and $S = 1/2$ spin states, the latter cannot themselves mix to first order. Since $S = 3/2$ spin state is not usual for ferric porphyrins, quantum mechanical spin-mixing is not a very commonly observed phenomenon and has in fact been indicated only recently in a few cases.

Bacterial ferricytochromes were discussed first in this context and were found to have 'anomalous' magnetic and spectral properties (Maltempo *et al* 1974; Ehrenberg and Kamen 1965; Tasaki *et al* 1967; Maltempo 1974). Some relevant magnetic data on these cytochromes are listed in table 1. Maltempo (1974) has attempted to interpret these results as being characteristic of substantial spin mixing between 4A_2 and 6A_1 states arising out of the configurations $(d_{xy})^2 (d_{xz}, yz)^2 (d_z)^1$ and $(d_{xy})^1 (d_{xz}, yz)^2 (d_z)^1 (d_{x^2-y^2})^1$ respectively. Similar spin mixing has recently been suspected in a number of synthetic ferric porphyrins (Dolphin *et al* 1978; Reed *et al* 1979; Boyd and Mitra 1980) which exhibit similar anomalous magnetic properties (see table 1). In all these cases the ground state appears to be predominantly $S = 3/2$ with some $S = 5/2$ character admixed into it, except in *rubrum* ferricytochrome *c'* where the ground state appears to be predominantly (68%) $S = 5/2$ with about 32% $S = 3/2$ admixed into it (Maltempo 1974).

We have been recently studying magnetic properties of metalloporphyrins especially iron porphyrins (Behere *et al* 1977, 1979, 1980; Behere and Mitra 1979, 1980; Boyd *et al* 1979). During the course of this work we synthesised an interesting iron(III) porphyrin, namely tetraphenylporphyrin iron(III) perchlorate diethanolate, $\text{TPPFe}(\text{ClO}_4)_2 \cdot 2(\text{C}_2\text{H}_5\text{OH}) \cdot \frac{1}{2}\text{CH}_2\text{Cl}_2$, which exhibits magnetic

Table 1. Magnetic moment of some spin-mixed iron(III) porphyrin.

| Compound | T (K) | $\bar{\mu}_{(g,m)}$ | Reference |
|--|-------|---------------------|--|
| Chromatium ferricytochrome <i>c'</i> | 293 | 5.15 | Maltempo <i>et al</i> (1974) |
| | 2.8 | 3.4 | |
| Rubrum ferricytochrome <i>c'</i> | 290 | 5.2 | Maltempo (1974); Tasaki <i>et al</i> (1967) |
| | 150 | 5.2 | |
| | 2.8 | 3.8 | |
| TPP Fe (ClO ₄) . $\frac{1}{2}$ xylene | 290 | 5.19 | Reed <i>et al</i> (1979); Boyd and Mitra (1980) |
| | 80 | 4.5 | |
| | 4.2 | 2.9 | |
| OEP Fe (ClO ₄) | 290 | 4.78 | Boyd and Mitra (1980) |
| | 80 | 4.25 | |
| | 4.2 | 3.58 | |
| TPP Fe(ClO ₄) ₂ (C ₂ H ₅ OH) $\frac{1}{2}$ CH ₂ Cl ₂ | 293 | 5.2 | Present work |
| | 150 | 5.2 | |
| | 80 | 5.2 | |
| | 3.5 | 3.6 | |

properties similar to the above bacterial heme protein. This paper describes results of our studies on this compound.

2. Experimental

2.1. Preparation of the compound

The compound was prepared by an adaptation of a general procedure available in literature (Adler *et al* 1970). Freshly prepared pure TPPFeCl was dissolved in benzene and shaken vigorously with aqueous sodium hydroxide to give dimeric μ -oxo-tetraphenylporphyrin iron(III). The μ -oxo-ferric complex was then purified by chromatography using a column of silica gel and eluting with benzene/ethanol mixture. A solution of the purified μ -oxo-ferric compound in dichloromethane was treated with several different aliquots of 2M aqueous perchloric acid in a separating funnel. The aqueous phase was discarded and the dichloromethane was gradually replaced by ethanol. The ethanol solution with a few drops of perchloric acid was allowed to evaporate slowly which yielded large lustrous dark air-stable crystals. Chemical analysis of the crystals gave following results; found : C = 64.79, H = 4.49, N = 6.3%; calculated for $C_{44}H_{28}N_4 Fe ClO_4 \cdot 2 C_2H_5OH \cdot \frac{1}{2} CH_2Cl_2$: C = 64.54, H = 4.58, N = 6.21%. Spectra of the compound in CH_2Cl_2 gave λ_{max} at 400, 518 and 669 nm.

2.2. Physical measurements

Magnetic susceptibility and Mössbauer of the sample between 80–300 K were measured using equipment built at Tata Institute of Fundamental Research, Bombay. The magnetic susceptibility below 80 K was measured at Orsay using a Faraday equipment.

3. Results and discussion

The magnetic susceptibility of the compound measured between 3.5 and 300 K is shown in figure 1. Some characteristic features of the data are also included in table 1 for comparison. At 293 K the magnetic moment per iron atom is 5.2 B.M. which is much lower than the expected value for a pure spin state $S = 5/2$. The magnetic moment remains nearly constant down to about 60 K, below which it slowly decreases reaching a value of 3.6 B.M. at 3.5 K. The lower value of the magnetic moment at room temperature may arise from (i) thermal spin equilibrium, say, between either $S = 5/2 \rightleftharpoons S = 1/2$ or $S = 5/2 \rightleftharpoons S = 3/2$; (ii) anti-ferromagnetic exchange interaction, or (iii) quantum mechanically mixed ground state. The near constant value of the magnetic moment above 60 K does not favour the first two possibilities (also see below). If the observed decrease in the magnetic moment is due to the spin state mixing, the most likely situation by comparison with other examples (table 1) would be the mixing between the close-lying $S = 5/2$ and $S = 3/2$ states.

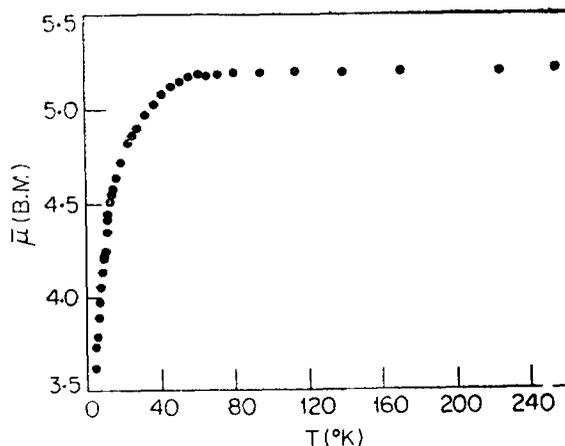


Figure 1. Temperature-dependence of average magnetic moment of the compound. The data were collected at external magnetic fields between 1–5 kOe.

More direct evidence in favour of such a proposal comes from the Mössbauer studies on this compound carried out at 300 and 77 K. Figure 2 shows the Mössbauer spectrum at 300 K of the polycrystalline sample matched against a standard Rh: Co⁵⁷ source. The spectrum at 77 K is almost identical to the above and hence is not reproduced here. The derived hyperfine interaction parameters namely the isomer shift (IS) and quadrupole splitting (ΔE_Q) are given in table 2 along with those of the related systems. The Mössbauer data clearly rule out the possibility of spin equilibrium in this compound since the spectra do not show the features characteristic of such a situation (Cox *et al* 1972; Richards *et al* 1968). On the other hand the broad asymmetric quadrupole split partners cannot be easily assigned to any single pure spin state using the well-known systematics of isomer shift and quadrupole interaction (Greenwood and Gibb 1970). The isomer shift of 0.28 ± 0.04 mm/sec with respect to iron metal indicates a high ($S = 5/2$) or intermediate ($S = 3/2$) ferric spin state while the quadrupole interaction $\Delta E_Q = 2.04 \pm 0.04$ mm/sec is much larger than usually observed for high spin ferric porphyrins (see table 2). In the absence of a pure $S = 3/2$ ferric porphyrin for comparison, the TPPFe(ClO₄) · ½ xylene with predominant $S = 3/2$ ground state could provide the closest example. It is evident that the ΔE_Q in TPPFe(ClO₄) · ½ xylene is much larger than in the present one and is temperature-dependent. In a pure $S = 3/2$ ground state (if it existed) ΔE_Q is expected to be still higher. Taking into account both the susceptibility and Mössbauer data an $S = 3/2$ ground state assignment for the present compound seems therefore unlikely.

We are thus led to the likely possibility that the ground state of the ferric ion in the present compound may be spin mixed between $S = 5/2$ and $S = 3/2$. To decide which of these two spin states may be the predominant ground state, we compare again our data with those on TPPFe(ClO₄) · ½ xylene and ferricytotochromes *c'*, the two spin-mixed ground state compounds for which detailed analysis of the data is available. TPPFe(ClO₄) · ½ xylene with a predominantly $S = 3/2$ ground state shows much larger quadrupole splitting as well as a much larger

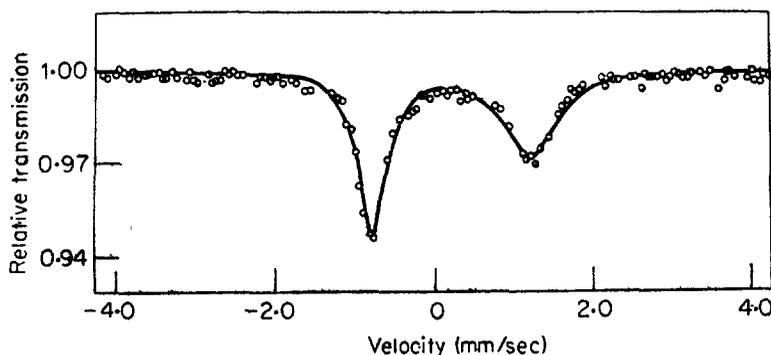


Figure 2. Mössbauer spectrum of the compound at room temperature.

Table 2. Mössbauer data of pure high spin and spin-mixed ferric porphyrins and proteins.

| Compound | $T(K)$ | I.S. mm/sec. | ΔE_Q mm/sec | Spin state |
|--|--------|--------------|---------------------|--|
| TPP Fe (ClO ₄) · 2 (C ₂ H ₅ OH) · ½ CH ₂ Cl ₂ | 300 | 0.28 ± 0.04 | 2.04 ± 0.04 | Spin-mixed with predomi- nantly high spin (present work) |
| | 77 | 0.35 ± 0.04 | 1.98 ± 0.04 | |
| Rubrum Ferricyto- chrome C' | 4.2 | 0.37 | 1.35 | Spin mixed with predomi- nantly high spin (Maltempo <i>et al</i> 1974) |
| TPP Fe (ClO ₄) · ½ xylene | 295 | 0.30 | 2.79 | Spin-mixed with predomi- nantly $S = 3/2$ spin state (Reed <i>et al</i> 1979) |
| | 195 | 0.34 | 3.17 | |
| | 77 | 0.38 | 3.48 | |
| | 4.2 | 0.38 | 3.50 | |
| OEP Fe (ClO ₄) | 295 | 0.37 | 3.16 | Spin mixed with predomi- nantly $S = 3/2$ spin state (Dolphin <i>et al</i> 1977) |
| | 115 | 0.37 | 3.52 | |
| | 4.2 | 0.29 | 3.57 | |
| TPP FeCl | 4.2 | 0.30 | 0.48 | Pure $S = 5/2$ spin state (Dolphin <i>et al</i> 1978) |

temperature dependence both in ΔE_Q and $\bar{\mu}$ above 80 K as contrasted to the nearly temperature independent ΔE_Q and $\bar{\mu}$ in the present compound. The most likely explanation of our result may thus be a predominantly $S = 5/2$ ground spin state with a close lying $S = 3/2$ spin state admixed into it. In this respect our compound is similar to the predominantly high spin *rubrum* ferricytochrome *c'* as against *chromatium* ferricytochrome *c'* which displays predominantly $S = 3/2$ ground state character. A more detailed comparison of our data with *rubrum* ferricytochrome *c'* is frustrated by the lack of detailed temperature-dependent magnetic and Mössbauer data for it. However ΔE_Q value of 1.35 mm/sec

at 4.2 K is not very different from the 1.98 mm/sec at 77 K for our sample when the effect of the difference in temperature is taken into account. Equally significant is the observation that $\bar{\mu}$ in the *rubrum* protein is nearly independent of temperature from room temperature down to 150 K (at which the data are reported), which is similar to the present compound. The *chromatium* ferricytochrome C' and other porphyrins listed in table 1 show a much larger temperature dependence above 80 K.

Harris (1966, 1968) has discussed in detail the theoretical behaviour of the spin mixed ground state in ferric heme systems. A simplification of the theory assumes the mixing through spin-orbit coupling of the high spin 6A_1 ground state with the closest lying 4A_2 excited state derived from $S = 3/2$ spin configuration. Calculation of magnetic moments based on such a model has been done by Maltempo (1974) for a range of the spin orbit coupling and the ${}^6A_1 - {}^4A_2$ energy separation. Maltempo's calculation reproduces our data of figure 1 at least qualitatively quite well for 6A_1 lying below 4A_2 ; an alternative possibility (i.e. 4A_2 lying below 6A_1) can be rejected quite unambiguously on the basis of these calculations.

An attempt at detailed fit of the $\bar{\mu}$ vs T data to the above model with a predominantly 6A_1 ground state was however not very successful. While the theory reproduces the trend in the $\bar{\mu}$ vs T curve, the exact fit is rather poor. This is not however surprising in view of the approximate nature of the model. A fuller analysis of the data must await a detailed single crystal susceptibility study which is now being planned.

Finally we would like to comment on some aspect of the Mössbauer spectrum (figure 2). The spectrum both at room temperature and 77 K shows unequal intensities for the two quadrupole split partners. For a randomly oriented polycrystalline sample one expects equal intensity and width for the two absorption peaks. There may be four possible reasons for the unequal intensity and width of the quadrupole partners: (i) texture or preferred orientation effect, (ii) absorber thickness effect; (iii) anisotropic Lamb-Mössbauer factor; and (iv) spin relaxation effect. To check (i) we made measurements on two randomly oriented sample absorbers and found identical intensity patterns. Reason (ii) can be easily ruled out since absorbers used in the present study were prepared with 10–15 mg/cm² of iron, a value quite usual in any typical experiment on iron complexes. Since there is no change in the ratio of the intensities of the quadrupole doublets with temperature, (iii) can also be ruled out. In fact spin relaxation effects appear to be therefore the main reason for the unequal width and intensities of the quadrupole doublets. Such a phenomenon has been previously observed in several $S = 5/2$ iron (III) porphyrins (Torrens *et al* 1972; McCann *et al* 1980). The broad line on the higher velocity side and a narrow line (with unequal intensity) on the lower energy side is indicative of a positive EFG (Blume 1965; Bhide and Date 1968). It is interesting to note that the sign of EFG in many iron(III) porphyrins is also positive (Dolphin *et al* 1978; Maricondi *et al* 1972).

4. Conclusion

The iron(III) porphyrin reported here appears to have spin-mixed ground state with predominantly $S = 5/2$ character. In this regard it resembles closely the

bacterial protein *rubrum* ferricytochrome *c'* which seems to be its closest magnetic analogue.

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